MINERALOGY BY X-RAY DIFFRACTION ON MARS: THE CHEMIN INSTRUMENT ON MARS SCIENCE LABORATORY.

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Introduction: To obtain detailed mineralogy information, the Mars Science Laboratory rover *Curiosity* carries CheMin, the first X-ray diffraction (XRD) instrument used on a planet other than Earth. CheMin has provided the first *in situ* XRD analyses of full phase assemblages on another planet.

The CheMin Instrument: CheMin uses a Co X-ray source, powder samples in piezo-driven vibrating cells, and a CCD detector in transmission geometry [1]. The CCD is cooled during operation and is energy-selective, with a quick read cycle that allows single-photon recognition and energy resolution of ~225 eV, sufficient to resolve diffracted Co Kα and Kβ. The CCD produces 2D diffraction patterns (Figure 1) that are processed into 1D Co Kα patterns with ~0.3° 2θ resolution. The 1D XRD patterns are analyzed for phase identification and quantification, using both Rietveld analysis and FULLPAT pattern fitting to calculate mineral proportions [2,3; Figure 2].

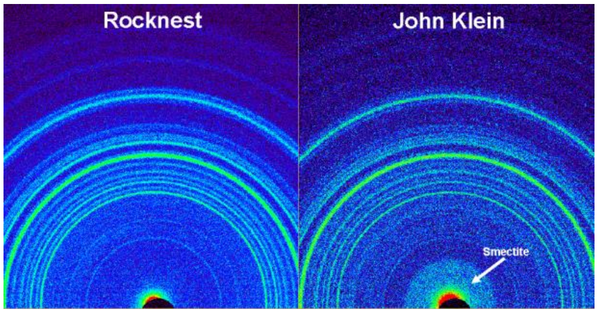

Figure 1: Colorized 2D CCD XRD patterns of an eolian sample (Rocknest) and a mudstone (John Klein). The region of smectite 001 diffraction, absent in Rocknest, is indicated in the John Klein pattern.

Samples: CheMin has collected XRD data from three different powder samples: scoop samples from an eolian deposit (Rocknest) and two drill samples from a mudstone (John Klein and Cumberland). The mudstone is informally named as the Sheepbed member of the Yellowknife Bay formation.

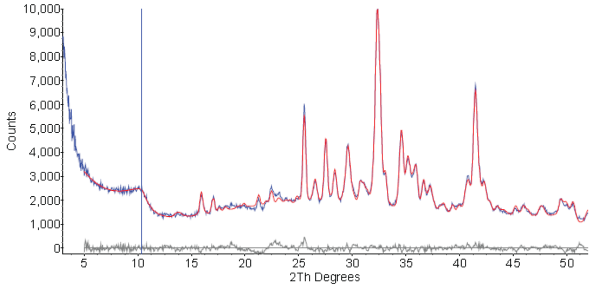

Figure 2: 1D XRD pattern of John Klein with observed (blue) versus calculated (red) patterns, and difference curve at the bottom (gray). Vertical line marks the smectite 001 diffraction maximum at ~10 Å.

The Rocknest eolian deposit is comprised of plagioclase (~An57), Fe-forsterite (~Fo62), augite, pigeonite, and magnetite; minor anhydrite and quartz; and sanidine, hematite and ilmenite near detection limits. A significant amount of the sample (~30%) is X-ray amorphous [2].

The mudstone samples, John Klein and Cumberland, contain smectite, plagioclase (~An44), augite, pigeonite, Fe-forsterite (~Fo51), orthopyroxene and magnetite; minor sanidine, bassanite, anhydrite, akaganeite and pyrrhotite; and quartz, hematite, ilmenite, pyrite and halite near detection limits. The mudstone also has a significant (~30%) X-ray-amorphous component [4]. The discussion that follows is focused on the mudstone mineralogy, which provides evidence for a potentially habitable lacustrine environment.

Clay Mineral Characterization: Clay minerals were not found in the Rocknest eolian deposit but comprise ~20% of the mudstone samples. Despite challenges of remote operation on Mars, details about the clay minerals can be extracted from CheMin diffraction data. Typical XRD analysis of clay minerals on Earth can include preparation of oriented mounts, control of relative humidity, cation-exchange treatments, glycolation, and heat treatment that are not possible on Mars. Moreover, the upper 2θ limit in CheMin is ~53°, precluding measurement of the 06*l* diffraction band (above 70° Co Kα) for determination of trioctahedral or dioc-

tahedral character. However, the less-commonly used position of the maximum in the 02*l* two-dimensional diffraction band is similarly related to the *b* unit-cell parameter and can be used to distinguish trioctahedral (~ 22.5° Co Kα; 4.59 Å) from dioctahedral (~23.1° Co Kα; 4.47 Å) minerals (Figure 3). The 02*l* bands in both mudstone samples suggest turbostratic stacking and we interpret these clay minerals as trioctahedral smectites.

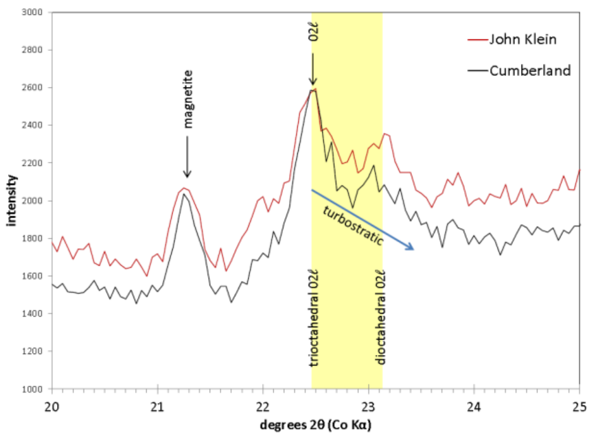

Figure 3: Comparison of smectite 02*l* diffraction bands in John Klein and Cumberland. Minor rise at about 23 degrees is associated with pyroxenes.

The XRD pattern of John Klein has a broad 001 peak at ~10 Å, corresponding with smectite or illite (Figure 2). Low K content, and a broad 001 peak with lack of other well-defined peaks, such as an 002 peak at 5 Å, argue against the presence of well-crystallized phyllosilicates such as mica or illite. In addition, peaks for kaolinite or chlorite-group minerals at 7 Å are absent. The low-angle region of the Cumberland XRD pattern has a second 001 peak at ~13.2 Å. This larger interlayer spacing in the Cumberland sample is of considerable interest because complete collapse of a smectite would be expected in the very dry conditions within CheMin (<1% RH). Possible explanations include H_2O retention in the interlayers by high hydration-energy cations, such as Mg or Ca, and partial pillaring via incipient chloritization. These possibilities are being addressed in the lab [5] and will be addressed in the field as more samples are analyzed at Gale crater.

Model of clay mineral and magnetite authigenesis: The 02*l* diffraction band maximum is very similar in John Klein and Cumberland and indicates a trioctahedral clay mineral such as ferrian saponite [6,7]. The mudstone has a surprisingly high abundance of magnetite (~4%) for a fine-grained (<50 μm [8]) sediment. High magnetite content and dearth of Fe-forsterite, relative to other mafic minerals from basaltic sources, has led to a model of authigenesis with smectite and magnetite produced by aqueous alteration of Fe-forsterite [4]. This model is supported by a lack of geochemical variation among the sediments of Yellowknife Bay relative to modal basaltic sources; such variation would be expected if the smectite and magnetite were transported [9].

Low salinity, moderate pH, and variable redox mineralogy: The crystalline salt content of the mudstone is low (<3%); moreover, when thin Ca-sulfate veins in the borehole walls are mapped it is clear that salts are concentrated in these late-diagenetic features and not in the mudstone matrix [4]. The salts are low-solubility Ca-sulfates; highly soluble Mg-sulfates, and Fe-sulfates indicative of acidic conditions, are absent. Among the crystalline phases, ferrous and ferric iron are both present, as well as sulfides and sulfates. From analog studies, Fe in the mudstone smectite is likely to be incompletely oxidized [6,7]. XRD evidence for both reduced and oxidized species is supported by evolved gas analyses [10]. From these multiple lines of evidence the mudstone has a mineral assemblage of variable redox states, moderate pH, and low salinity that could support a microbial community [7].

A post-Noachian lacustrine system: A current model for clay mineral occurrences on Mars relates them principally to the southern highlands, where they remain as vestiges of a wet environment that ended ~4 Gy ago as a drier system evolved, dominated by sulfates rather than clay minerals [11]. The oldest sediments within Gale crater are probably of Early Hesperian age [8]; data from Gale crater may thus extend the proposed transition from potentially habitable to less favorable environments to a later time. In several months, *Curiosity* will be at the central mound of Gale crater where abundant clay minerals have been recognized from orbit [12]. *Curiosity* will traverse through the phyllosilicate stratigraphy and into overlying "drier" sulfate strata. Records of a major shift in ancient Mars environments might be found at Gale crater.

References: [1] Blake D. et al. (2012) *Space Sci. Rev.*, *170*, 341-399. [2] Bish D.L et al. (2013) *Science*, *341*, 10.1126/science.1238932. [3] Chipera S.J. and Bish D.L. (2002), *J. Appl. Cryst.*, *35*, 744-749. [4] Vaniman D.T. et al. (2014) *Science*, *343*, 10.1126/science.1243480. [5] Rampe E.B et al. (2014) *45th LPSC*, abst. 1890. [6] Morris R.V. et al., this conference. [7] Treiman et al., (in press) *Am. Min*. [8] Grotzinger J.P. et al. (2014) *Science*, *343*, 10.1126/science.1242777. [9] McLennan S.M. et al., *Science*, *343*, 10.1126/science.1244734. [10] McAdam A.C. et al., this conference. [11] Bibring J.-P. et al. (2006) *Science*, *312*, 400-404. [12] Milliken R.E. et al. (2010) *GRL*, *37*, 10.1029/2009GL041870.